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Structural correlations of $Ge_{20}Se_{80-x}Te_x$ glasses based on reverse Monte Carlo simulation

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ABSTRACT

Bulk chalcogenide $Ge_{20}Se_{80-x}Te_x$ (where $x = 0$, 10, 20 and 30 at.%) glasses were prepared using the melt-quench technique. The total structure factors of these alloys are obtained from the X-ray scattering data in the momentum transfer interval $0.61 \leq K \leq 16.45$ Å^{-1}. From reverse Monte Carlo (RMC) simulations of the X-ray scattering data, the short and intermediate-range order parameters are obtained. The simulations are useful to compute the partial pair distribution functions, $g_{ij}(r)$, and the partial structure factors, $S_{ij}(K)$. In Te-rich glass, the first sharp diffraction peak (FSDP) appears as a shoulder, instead of a peak for others, confirms that Se–Se bonds in addition to Ge–Ge bonds are responsible for the intermediate-range order inside these glasses. The partial coordination numbers and the bond angle distributions within the first coordination shell have been calculated. The ratio of the first to second peak positions (r_1/r_2) and the corresponding bond angle (Θ) have confirmed that the $Ge(Se_{1/2})_4$ tetrahedra, connected by Se–Se chains, can be considered as the main building units inside the investigated glasses.

1. Introduction

The physical properties of materials are significantly dependent on their atomic structure, so measurements of the experimental data related to structure are fundamental to material science. For crystalline materials, numerous methods were developed for producing or refining models of the crystals structure based on the experimental data. However, non-crystalline materials are of equal, if not greater, technological importance, yet our structural understanding is still relatively primitive and few methods of structural modeling have been developed.

Amorphous semiconductor materials like chalcogenide glasses present a great potential for applications in technological devices, such as optical fibers, memory materials and switching devices, but their use is limited due to several factors. One of them is the difficulty in obtaining information about atomic structures, which define the short-range order (SRO) and the intermediate-range order (IRO) of the alloy. In this context, the structures of amorphous Ge_xSe_{100-x}, in particular $Ge_{20}Se_{80}$, have been extensively studied by several experimental techniques like X-ray diffraction [1–3], neutron diffraction [4,5] and Raman scattering [6]. The structure unit in the glass is $Ge(Se_{1/2})_4$ tetrahedra connected through Se–Se chains.

Reverse Monte Carlo (RMC) simulation [7,8] represents, when used carefully, a powerful tool to extract some information of intermediate and extended-range scale in glassy materials. It assembles three-dimensional atomic configurations using experimental diffraction data implicitly in the simulation. The intimate connection between computational and experimental processes means that the better quality and higher resolution of the experimental data, the more reliable RMC model of a network structure for vitreous materials. The RMC method is an inverse problem in which the experimental data are enforced to build atomic configurations that have the desired structural and electronic properties. The main point is to set up a generalized function containing as much information as possible, and then optimize the function for generating configurations toward exact agreement with the experimental data.

Addition of Te to $Ge_{0.2}Se_{0.8}$ glass improves its IR transmission and reduces the energy losses due to multi-phonon absorption [9]. A number of papers have appeared in literature reporting the electrical [10,11] and photoelectrical properties [12–14] and crystallization kinetics [15–17] of Ge–Se–Te glasses. To our best knowledge, there are insufficient studies on the structural correlations of the above system. Therefore, the present article is mainly devoted to the structure correlations of the $Ge_{20}Se_{80-x}Te_x$ (where $0 \leq x \leq 30$ at.%) alloys.

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Table 1
Different configuration parameters and the number of the constituent atoms used in the RMC simulation program.

	M1	M2	M3	M4
Box edge (Å)	23.597	23.745	23.897	24.053
Density (atom/Å^3)	0.0381	0.0373	0.0366	0.0359
Ge atoms	800	800	800	800
Se atoms	3200	2800	2400	2000
Te atoms	–	400	800	1200

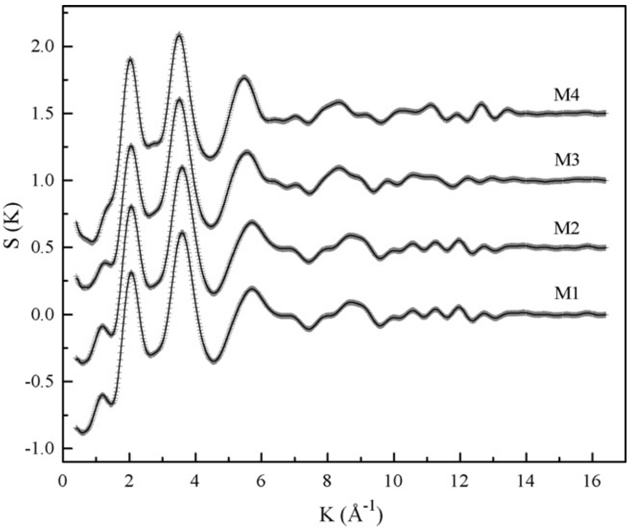

Fig. 1. Experimental X-ray diffraction structure factors (+symbol) together with the results of RMC simulations (solid lines) of the $Ge_{20}Se_{80-x}Te_x$ (where $x = 0, 10, 20$ and 30 at.%) glasses.

2. Theoretical background

Three-dimensional arrangement of N atoms is placed into a cubic cell with periodic boundary conditions. The atomic number density (ρ) should be the same as the experimental value. The positions of the atoms are chosen randomly. The partial pair distribution function [7] can be calculated from the initial configuration by

$$g_{ij}^{Co}(r)=\frac{n_{ij}(r)}{4\pi r^2 dr\rho c_i} \tag{1}$$

where the superscripts C and o mean 'calculate' and 'old', respectively, c_i is the concentration of atoms type i and $n_{ij}(r)$ is the average number of atoms type j located at distance between r and $r + dr$ from a central atom of type i. Fourier transform of $g_{ij}^{Co}(r)$ to reciprocal space yields the partial static structure factor:

$$S_{ij}^{Co}(K)=\rho\int_0^\infty 4\pi r^2(g_{ij}^{Co}(r)-1)\frac{\sin Kr}{Kr}dr \tag{2}$$

where K (=$4\pi\sin\theta/\lambda$) is the momentum transfer. The total structure factor is calculated as follows:

$$S^{Co}(K)=\sum_{i,j} c_i c_j f_i(K) f_j(K)(\,S_{ij}^{Co}(K)-1) \tag{3}$$

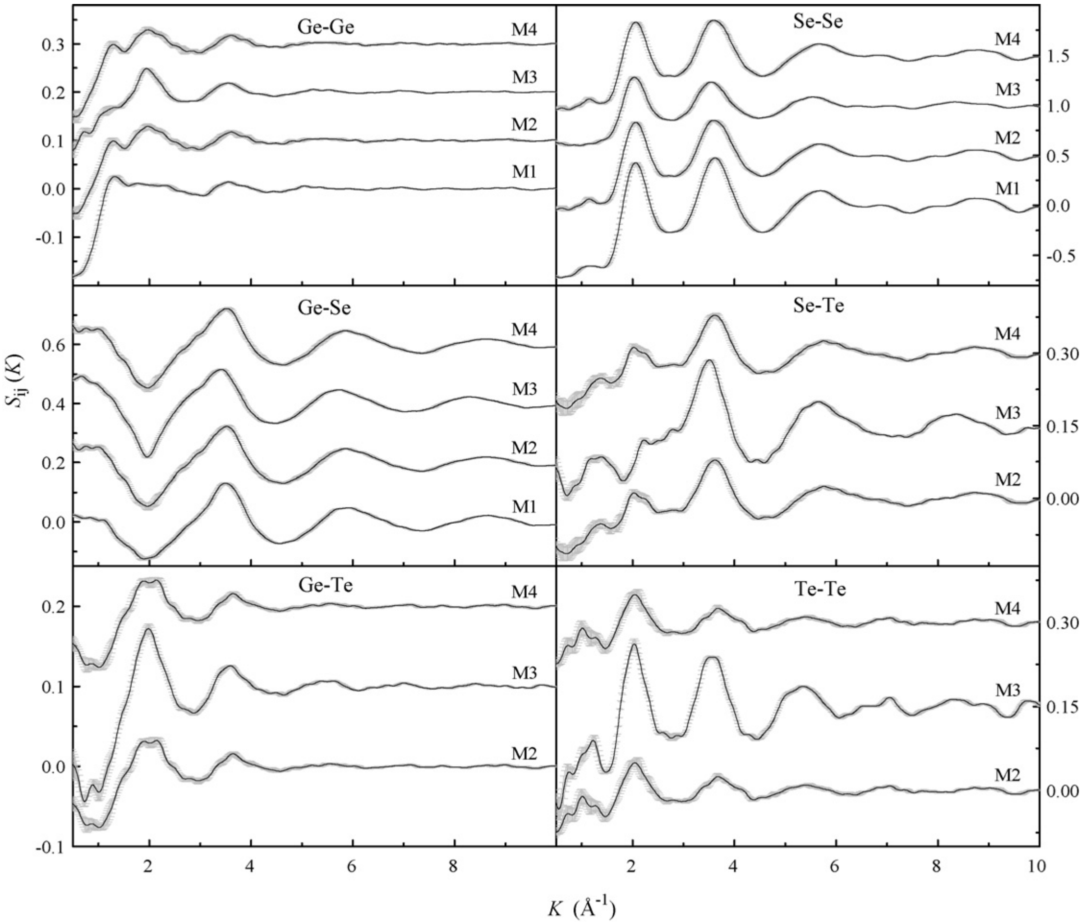

Fig. 2. Partial scattering factors, $S_{ij}(K)$, obtained from the present RMC simulation for the $Ge_{20}Se_{80-x}Te_x$ (where $x = 0, 10, 20$ and 30 at.%) glasses.

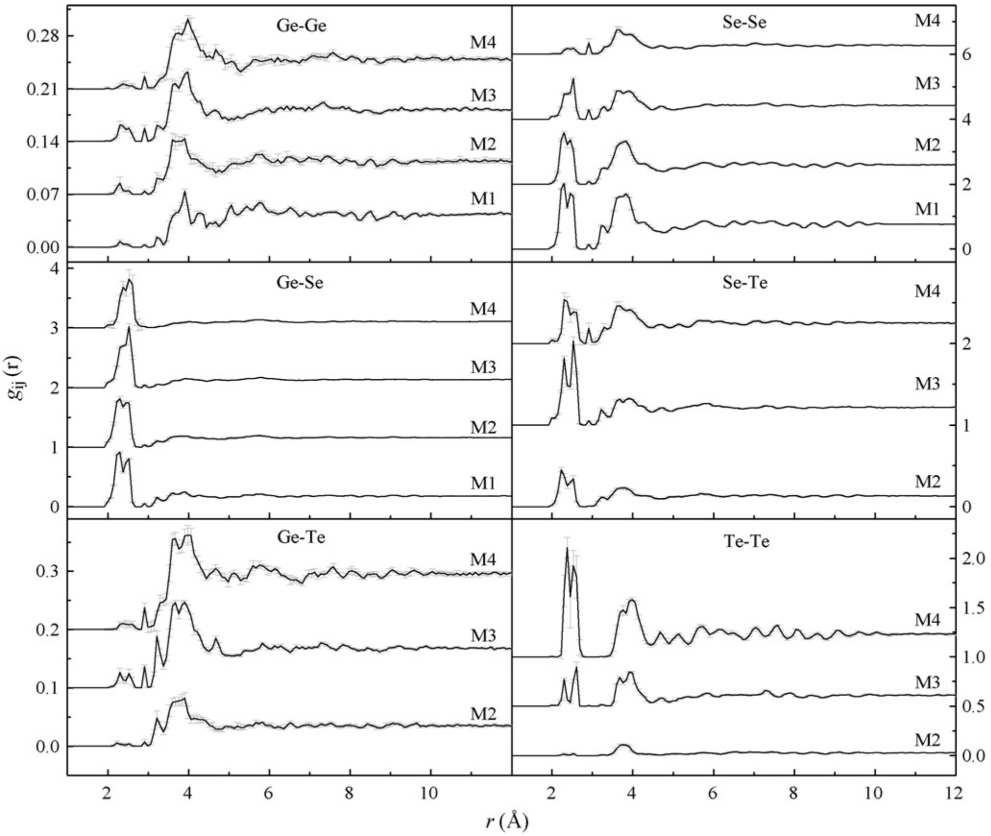

Fig. 3. Partial pair distribution functions, $g_{ij}(r)$, obtained from the present RMC simulation for the $Ge_{20}Se_{80-x}Te_x$ (where $x = 0$, 10, 20 and 30 at.%) glasses.

where $f_i(K)$ is the atomic scattering factor of atom type i. The difference between the experimental total structure factor, $S^E(K)$, and that calculated from the configuration is given by

$$\chi_o^2 = \sum_{i=1}^{m} \frac{(S^{Co}(K_i) - S^E(K_i)^2}{\sigma^2(K_i)} \tag{4}$$

where the sum is taken over the m experimental points and σ represents the experimental error. One atom moves at random but if it approaches another atom closer than the cut-off distance, the move is rejected. Otherwise, a new atom is chosen with acceptable move. Then, the new values of the partial pair distribution functions, partial structure factors, and the total structure factor can be calculated. The new value of $S^{Cn}(K)$ gives a new difference:

$$\chi_n^2 = \sum_{i=1}^{m} \frac{(S^{Cn}(K_i) - S^E(K_i)^2}{\sigma^2(K_i)} \tag{5}$$

where n means 'new'. If $\chi_n^2 < \chi_o^2$, the move is accepted and the new configuration becomes the old one. If $\chi_n^2 > \chi_o^2$, it is accepted with probability $\exp(-(\chi_n^2 - \chi_o^2)/2)$. Otherwise it is rejected. As the number of accepted atom moves increases, χ^2 will initially decrease until it reaches an equilibrium value. Thus, the atomic configuration corresponding to the equilibrium should be consistent with the experimental total structure factor within the experimental error. From the equilibrium values of the partial pair distribution function, one can calculate the partial coordination number, partial inter-atomic distance and the bond angle distribution.

3. Experimental technique

Bulk $Ge_{20}Se_{80-x}Te_x$ (where $x = 0$, 10, 20 and 30 at.%) chalcogenides were prepared using the melt-quench technique. High purity Ge, Se, and Te elements (99.999%) were, weighed according to their atomic percentages, charged into chemically cleaned silica tubes and then sealed under vacuum of $\approx 1.33 \times 10^{-3}$ Pa. The ampoules were put into a furnace where the temperature was gradually increased to 1300 K at heating rate of 3–4°/min. The ampoules were frequently rocked for 24 h at the highest temperature to make the melt homogeneous. The quenching was done in ice cold water. The glassy state of the quenched specimens was confirmed by X-ray diffraction technique. X-ray diffraction experiment was done using a PW3050/60 X'Pert PRO Standard Resolution Goniometer, with the Molybdenum anode ($\lambda = 0.7179$ Å). The experiment was done in the scattering angle range $4 \le 2\theta \le 140°$ in steps of 0.5°, which corresponds to K-range $0.61 \le K \le 16.45$ Å^{-1}. From hereafter and seeking simplicity, the symbols M1, M2, M3, and M4 will be used to represent the $Ge_{20}Se_{80}$, $Ge_{20}Se_{70}Te_{10}$, $Ge_{20}Se_{60}Te_{20}$ and $Ge_{20}Se_{50}Te_{30}$ glasses, respectively.

4. RMC simulation details

The starting point in RMC simulation [18] is to randomly generate the configuration distribution of $N = 4000$ atoms inside a cubic box. The portions of Ge, Se and Te atoms in the assumed configuration will vary according to their atomic percentages. As shown in Table 1, the number of Ge atoms is the same (=800 atom) for the investigated alloys, while the number of Te atoms increases on the expense of Se content. Accordingly, the calculated specimen density decreases with increasing edges of the cubic box. RMC simulation runs for 20 h using the total structure factor fit under the coordination constraints and a minimum approach distance of 1.96 Å for any atoms pair. When χ^2 oscillates around an equilibrium value, a three-dimensional molecular image of a disordered structure can be obtained. In order to get an accurate image, the average of five simulation trials was taken for each composition.

Table 2
The partial coordination number ($\eta_{ij} \pm 0.02$) and the partial atomic distances ($r_{ij} \pm 0.04$) in the first coordination shell of the investigated $Ge_{20}Se_{80-x}Te_x$ glasses. The numbers between brackets are the values obtained from CONM model.

	M1		M2		M3		M4	
	η_{ij}	r_{ij}	η_{ij}	r_{ij}	η_{ij}	r_{ij}	η_{ij}	r_{ij}
Ge–Ge	0.02 (0)	2.36	0.04 (0)	2.29	0.09 (0)	2.40	0.05 (0)	2.43
Ge–Se	4.05 (4)	2.33	3.93 (4)	2.35	3.96 (4)	2.44	3.92 (4)	2.46
Ge–Te	–	–	0.01 (0)	2.31	0.06 (0)	2.40	0.07 (0)	2.44
Se–Ge	1.01 (1)	2.33	1.12 (1.14)	–	1.32 (1.3)	–	1.57 (1.6)	–
Se–Se	1.94 (1)	2.31	1.68 (0.57)	2.35	1.32 (0)	2.43	0.50 (0)	2.44
Se–Te	–	–	0.31 (0.29)	2.33	0.79 (0.67)	2.43	0.67 (0.4)	2.43
Te–Ge	–	–	0.02 (0)	–	0.06 (0)	–	0.05 (0)	–
Te–Se	–	–	2.14 (2)	–	2.37 (2)	–	1.12 (0.67)	–
Te–Te	–	–	0.04 (0)	2.39	0.43 (0)	2.50	1.45 (1.33)	2.45

The chemical order network model (CONM) constraints have been used for the first coordination sphere. Accordingly, the bonds are formed in the sequence of decreasing bond energies until all available valences of the atoms are saturated [19]. Based on Pauling [20] equation, the bond energies of heteronuclear are greater than those of homonuclear bonds and the energies of the Ge–Se, Se–Te and Ge–Te bonds are 49.42, 44.18 and 35.47 kcal/mol, respectively. Finally, the experimentally obtained data of the partial and total coordination numbers are compared with the simulated RMC and the calculated CONM values.

Table 3
The total coordination number in the first shell obtained from RMC simulation, CONM calculation and conventional (Fourier) data.

	First neighbors coordination number		
	RMC	CONM	Fourier
M1	3.15 ± 0.02	2.36	2.90 ± 0.2
M2	3.08 ± 0.02	2.32	2.91 ± 0.2
M3	3.33 ± 0.02	2.28	3.14 ± 0.2
M4	2.90 ± 0.02	2.32	2.84 ± 0.2

5. Results and discussion

Fig. 1 shows the simulated total structure factors of the investigated M1($Ge_{20}Se_{80}$), M2($Ge_{20}Se_{70}Te_{10}$), M3($Ge_{20}Se_{60}Te_{20}$), and M4($Ge_{20}Se_{50}Te_{30}$) glasses in compare with the corresponding experimental curves up to $K = 16.45\,\text{Å}^{-1}$. A good agreement between the simulated and experimental data can be easily seen. For the binary glass, the first sharp diffraction peak (FSDP) located at $K = 1.2\,\text{Å}^{-1}$ is very close to that reported previously by Rao et al. [5]. FSDP, which is commonly observed in covalently bonded amorphous materials, implies the presence of intermediate-range order caused by connection of the structural units. Increasing Te content on the expense of Se in Te-rich glasses, in spite of $f_{Te} > f_{Se}$, reduces the intensity of the FSDP to the point that a shoulder rather than a peak has appeared in the total structure factor. Accordingly, it seems reasonable to assume, as previously reported by Wang et al. [3], that the medium range order is resulted from ordered sequences of Se–Se in addition to Ge–Ge bonds.

Fig. 2 shows the partial structure factors, $S_{ij}(K)$, obtained from the present RMC simulations. The partial structure $S_{Ge-Ge}(K)$ and $S_{Se-Se}(K)$ factors having tiny peaks around $1.2\,\text{Å}^{-1}$ confirm that Ge–Ge and Se–Se bonds are behind the presence of the FSDP. The partial structure $S_{Ge-Ge}(K)$, $S_{Ge-Se}(K)$ and $S_{Se-Se}(K)$ factors are nearly the same for all glasses, while for those with Te atoms as a partner show appreciable changes with increasing Te content. The partial pair distribution, $g_{ij}(r)$, functions for the investigated alloys are shown in Fig. 3. In fact, most of the important structural parameters such as the coordination number, inter-atomic distance and bond angle distribution can be deduced from the partial pair distribution function. It is easily seen from the above figure that the partial pair distribution $g_{Se-Se}(r)$ and $g_{Te-Te}(r)$ data show peaks around the first coordination sphere indicating the existence of homo-polar bonds in the structural units, which is consistent with the previous results [1,7]. Table 2 summarizes the simulated values of the partial coordination numbers and the partial atomic distances inside the investigated glasses. The total coordination numbers obtained from RMC simulation, CONM calculation and from the experimental measurements are listed in Table 3. The existence of homo- (or wrong) bonds such as Ge–Ge, Se–Se and Te–Te, as indicated from their partial pair distributions, can be a reason for high values of the simulated coordination numbers in compare with those given from CONM model.

Based on the partial pair distribution functions shown in Fig. 3, the bond angle can be calculated from ratio of the first to second peak positions (r_1/r_2). The distances ratio, averaged over all compositions, is found to be 0.622. A result which is very close to a value of

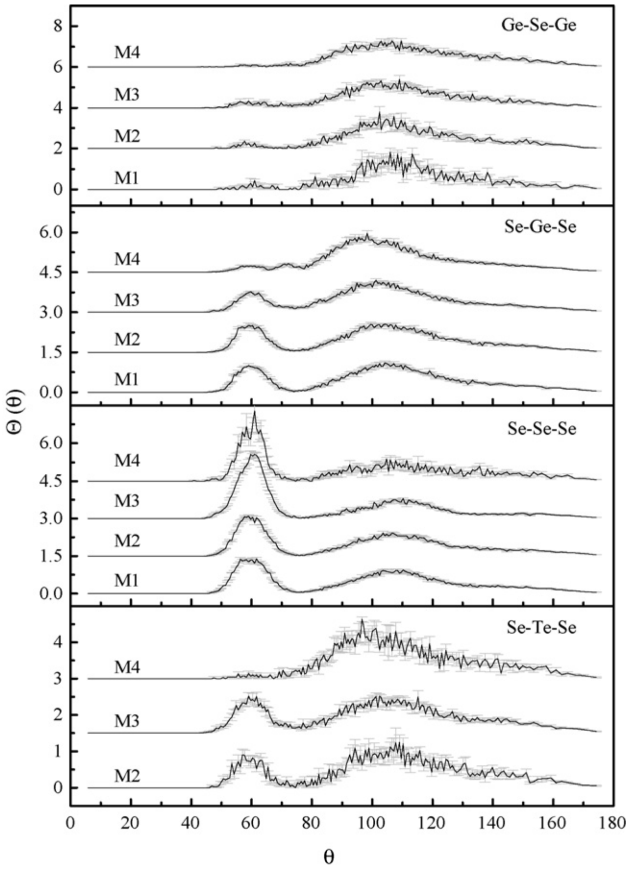

Fig. 4. Bond angle distribution functions, $\Theta(\theta)$, obtained from RMC simulation.

0.612 expected for perfect tetrahedral coordination, indicating the presence of tetrahedral $Ge(Se_{1/2})_4$ structural units in the studied alloys. It is interesting to investigate the angular distribution of the bonds between first-neighbor atoms. Bond angle distribution functions $\Theta(\theta)$ obtained from the present RMC simulation are shown in Fig. 4. $\Theta_{\text{Se–Ge–Se}}(\theta)$ function presents a main peak at around 105°, which is near the ideal tetrahedral angle of 109°, and unphysical small peak appeared at 60°. $\Theta_{\text{Se–Se–Se}}(\theta)$ function has main peaks at 60°, which equals the internal Se–Se–Se angles in perfect tetrahedral. The above two bond angle functions suggest that the present amorphous alloys are constructed from tetrahedral units. A sub peak around 109° in $\Theta_{\text{Se–Se–Se}}(\theta)$ implies the existence of homopolar bond in tetrahedral units. A similar, but a complementary, trend can be observed between both $\Theta_{\text{Se–Te–Se}}(\theta)$ and $\Theta_{\text{Se–Se–Se}}(\theta)$ functions, which means that decreasing the first function in one point corresponds to an increase of the second function with Te content. From the similarity of the bond angle distributions, one can conclude that Se substitution by Te atoms does not introduce any disturbance in the structural network of the investigated glasses.

6. Conclusions

The experimental total structure factors of the chalcogenide $Ge_{20}Se_{80-x}Te_x$ (where x = 0, 10, 20 and 30 at.%) glasses have shown an excellent agreement with those obtained from RMC simulation of their X-ray scattering data in the momentum transfer interval $0.61 \leq K \leq 16.45\,\text{Å}^{-1}$. The structural information of the short-range order (SRO) and the intermediate-range order (IRO) are obtained from the simulated RMC values of the partial pair distribution functions and the partial structure factors. Increasing Te content on the expense of Se atoms does not affect significantly the short-range order, while appreciable changes in the intermediate-range order through the first sharp diffraction peak have been occurred. Se–Se bonds in addition to Ge–Ge bonds are responsible for the intermediate-range order inside these glasses. The ratio of the first to second peak positions (r_1/r_2) and the corresponding bond angle (Θ) have confirmed that the $Ge(Se_{1/2})_4$ tetrahedra, connected by Se–Se chains, can be considered as the main building units inside the investigated glasses.

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